TITLE:

<Fundamental Material Properties> Molecular Dynamic Characteristics

AUTHOR(S):

CITATION:

<Fundamental Material Properties> Molecular Dynamic Characteristics. ICR Annual Report 2004, 10: 24-25

ISSUE DATE:

2004-03

URL:

http://hdl.handle.net/2433/65403

RIGHT:

京都大学学術情報リポジトリ KURENAI 紅 Kyoto University Research Information Repository

Fundamental Material Properties
- Molecular Dynamic Characteristics -

http://modych.kuicr.kyoto-u.ac.jp

Prof
HORII, Fumitaka
(D Eng)

Assoc Prof
KAJI, Hironori
(D Eng)

Instr
HIRAI, Asako
(D Eng)

Techn
OHMINE, Kyoko

Students

KUSAKA, Yasunari (D3)
ONOYAMA, Goro (M2)
TSUJITANI, Kouji (M2)
IKUNO, Masaya (M1)
TSUKAMOTO, Naoki (M1)
OKAZAKI, Hiroyuki (UG)
SUZUKI, Furitsu (UG)
YAMADA, Tomonori (UG)

Associate Instructors (pt)

Dr TSUNASHIMA, Yoshisuke
Dr ISHIDA, Hiroyuki

Visitors

Dr AMORNSAKCHAI, Taweechai	Mahidol University, Tailand, 17 March - 11 April, 2003
Prof HU, Shaohua	Donghua University, China, 22 April - 25 April, 2003
Prof LAUPRETRE, Francoise	CERMAV, France, 4 May - 17 May, 2003
Mr CHAIYUT, Nattawut	Mahidol University, Tailand, 19 May - 18 August, 2003

Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of highly organized polymer materials in the different states by high-resolution solid-state NMR, electron microscopy, X-ray diffractometry, and so on, in order to develop high-performance and high-functionality polymer materials such as organic electron luminiscence devices and inorganic-organic molecular hybrids. The structure formation process of bacterial cellulose is also charcterized in detail and new types of cellulosic nanohybrid materials are examined to develop in different stages of the biosynthesis.

Research Activities (Year 2003)

Presentations

Nanoassembly Structure and Its Changes of Bacterial Cellulose, Horii F, 225th ACS National Meeting, 24 March (Invited).

Multidimensional Multiple-Quantum NMR Analyses of Local Structures in Solid Polymers, Kaji H, 52th Annual Meeting, Soc. Polym. Sci., Jpn., 28 May (Invited).

AFM Observation of Band-like Cellulose Assemblies Produced by *Acetobacter Xylinum*, Hirai A, Tsujii Y, Tsuji M, Horii F, 52th Annual Meeting, Soc. Polym. Sci., Jpn., 28 May.

Structure of Nano-Assemblies of Bacterial Cellulose Produced in the Presence of Fluorescent Brightener with Different Concentrations, Tsujitani K, Hirai A, Horii F, Tsuji M, Annual Meeting, Cellulose Soc. Jpn, 18 July.

Solid Structure and Dynamics of Polymers - Recent Research Progress, Horii F, 52th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 24 September (Invited).

Structure of Band-like Cellulose Assemblies Produced by *Acetobacter Xylinum*, Hirai A, Horii F,Tsujii Y, Tsuji M, 52th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 24 September.

Structure Analyses of Polymer Organic EL Materials by Solid-State NMR Spectroscopy, Kaji H, Onoyama G, Tsukamoto N, Horii F, 52th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 25 September.

Structures and Dynamics of Carrier Transport Materials in Organic EL Devices, Kaji H, Tsukamoto N, Yamada T, Horii F, 42th NMR Conf. Jpn., 26 November.

Grants

Kaji H, Higher Order Structures and Optical Properties of Light-Emitting Polymeric Materials, PRESTO, Japan Science and Technology Agency, 1 November 2002 - 31 October 2005.

Hirai A, Preparation and Structural Analysis of Bacterial Cellulose/Natural Inorganic Nanocomposites, Grant-in Aid for Scientific Research (C)(2), 1 April 2003 - 31 March 2005.

Sine-Modulated Two-Dimensional Pure Exchange Solid-State NMR as a Tool for Characterizing Dynamics in Solids

We present a simple two-dimensional (2D) solid-state exchange NMR method to suppress significant undesirable diagonal signals, termed 2D sine-modulated pure exchange (2D SIMPREX). Two delays, τ, incorporated in standard 2D exchange experiments modulate the 2D spectra with $\sin\{(\Omega_1-\Omega_2)t\}$, where Ω_1 and Ω_2 are precession frequencies corresponding to y- and x-axes of 2D spectra, respectively. A demonstration for dimethyl sulfone (DMS), $(CH_3)_2SO_2$, is shown in Fig. 1. The diagonal signals are successfully suppressed by incorporating the sine-modulation, which results in clear detection of 108° reorientation motion of CH_3 groups in DMS. Another demonstration is given for polyethylene, by combining this technique with magic angle spinning. Not only the exchange signals between the crystalline and noncrystalline components but also those among the noncrystalline components in different states, which could not be detected so far, are clearly observed. The 2D SIMPREX techniques enable us to efficiently identify and analyze the dynamics in solid materials, which are difficult to be detected so far due to the overlap with huge diagonal artifacts.

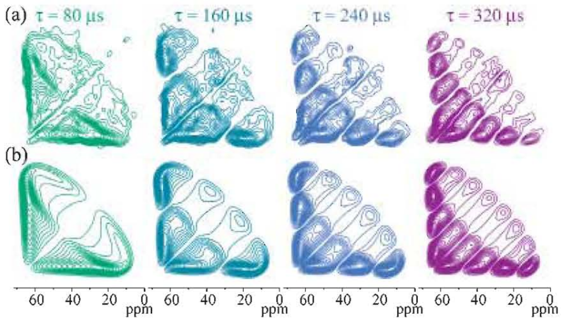
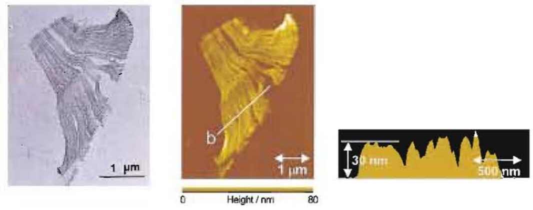


Fig. 1 (a) Experimental 2D SIMPREX spectra of DMS at 23 °C. (b) Simulated spectra for (a) with reorientation angle of 108°. Both the positive and negative signals are shown as solid lines. The mixing time is 50 ms.

AFM Observation of Cellulose Assemblies Produced by *Acetobacter Xylinum*

TEM, AFM and X-ray diffraction studies revealed the crystal structure and higher order structures of cellulose assemblies produced by *Acetobacter xylium* under different culture conditions. TEM, however, gave only two-dimensional structural information of the specimen. Recently, we have succeeded in obtaining three-dimensional structural information by combining AFM and TEM observations. Fig. 2a shows a TEM photograph of band-like cellulose assembly on the TEM grid. Fig.2b shows an AFM image of the same band-like cellulose assembly on the same grid. The height of band-like cellulose assemblies was estimated to be 20-30 nm from their AFM height profiles as shown in Fig. 2c. The crystallite sizes in the band-like cellulose assembly were estimated from the X-ray diffraction analysis. A structural model of the band-like cellulose assembly was proposed on the basis of these results.



(a) (b) (c)

Fig. 2 (a) TEM photo of band-like cellulose assembly. (b) AFM image of band-like cellulose assembly on the TEM grid. (c) Height profile along the line b in Fig. 2b.

Inorganic-Organic Molecular Hybrid Materials with Polyoxometalate Cores

Antimonate, a kind of polyoxometalate, is expected to use as core or building block for inorganic-organic nanohybrid materials because surface oxygens have high basicity. $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion (**1**) was successfully prepared by the reaction of octaantimonate $[Sb_8O_{12}(OH)_{20}]^{4-}$ with *t*-butyl dimethyl silanol and the detailed structure was clarified by solid-state NMR. In contrast, other silanols seem not to react with octaantimonate in a similar way and the specific antimonate frame may be destroyed. Substitution reactions were, therefore, examined between the silanol residues and other silanols for anion **1**. As a result, two vinyl silanols $C_2H_3Si(CH_3)_2OH$ were found to be introduced at the top and bottom sites as shown in Fig. 3, which was obtained by single-crystal X-ray diffractometry. Further reactions associated with the vinyl groups of anion (**2**) are in progress.

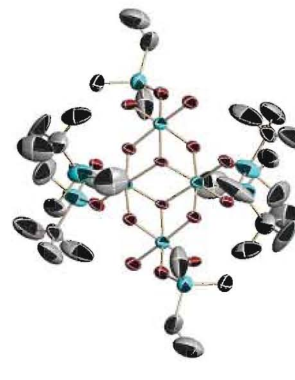


Fig. 3 Structure of $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(C_2H_3)\}_2\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_4]^{2-}$ anion (**2**).